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Adverse reactions to orthodontic materials

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Abstract: Adverse effects can arise from the clinical use of orthodontic materials, due to the release of constituent substances (ions from alloys and monomers, degradation by-products, and additives from polymers). Moreover, intraoral aging affects the biologic properties of materials. The aim of this review is to present the currently identified major adverse effects of the metallic and polymeric components found in orthodontic appliances and materials. Corrosion in metallic orthodontic attachments releases metal ions, mainly iron, chromium, and nickel. The latter has received the greatest attention because of its reported potential for an allergic response. The formation of an oxide layer may inhibit the outward movement of ions, thereby acting as an obstacle for release. Titanium alloys have superior corrosion resistance than stainless steel. The efficiency of polymerisation is considered an essential property for all polymers. A poor polymer network is susceptible to the release of biologically reactive substances, such as bisphenol-A (BPA), which is capable of inducing hormone-related effects. The close proximity of a light-curing tip to the adhesive, pumice prophylaxis after bonding, indirect irradiation and mouth rinsing during the first hour after bonding may decrease BPA release. The adverse effects of some orthodontic materials should be considered during material selection and throughout orthodontic treatment, in order to minimise possible undesirable implications.

DOI: <https://doi.org/10.1111/adj.12473>

Posted at the Zurich Open Repository and Archive, University of Zurich

ZORA URL: <https://doi.org/10.5167/uzh-149198>

Journal Article

Accepted Version

Originally published at:

Sifakakis, Iosif; Eliades, Theodore (2017). Adverse reactions to orthodontic materials. *Australian Dental Journal*, 62(S1):20-28.

DOI: <https://doi.org/10.1111/adj.12473>

Adverse reactions to orthodontic materials

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Australian Dental Journal 2017;62 (Supplement 1):20-28

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Abstract

Adverse effects arise from the clinical use of orthodontic materials, favoring release of substances (ions from alloys and monomers, degradation by-products, and additives from polymers). Moreover, intraoral aging affects the biologic properties of materials. The aim of this review is to present the major adverse effects of the metallic and polymeric components of the orthodontic appliances.

Various types of corrosion in the metallic attachments release metal ions, mainly iron, chromium, and nickel. The latter has received the most attention because of its reported potential for hazardous effects. The formation of oxide layer may inhibit the outward movement of ions, thereby acting as an obstacle for release. Ti alloys have superior corrosion resistance than stainless steel.

Polymerization efficiency is considered an essential property for all polymers. A poor polymer network is susceptible to the release of biologically reactive substances, such as bisphenol-A (BPA), which is able to induce hormone-related effects. Close proximity of the light-cure tip to the adhesive, pumice prophylaxis after bonding, indirect irradiation and mouth rinsing during the first hour after bonding may decrease BPA release.

As with dental biomaterials, some orthodontic materials are associated with adverse effects, which should be considered during material selection and throughout orthodontic treatment, in order to minimize their undesirable implications.

Key words: adverse reactions, orthodontic materials, side effects

Introduction

Orthodontic appliances, fixed or removable, consist of metallic, ceramic and polymeric components and are considered non cytotoxic, under certain conditions¹. However, alteration of their biologic properties is anticipated after clinical use and adverse effects arise, including release of substances (ions from alloys and monomers, degradation by-products, and additives from polymers).

Currently, orthodontists principally use stainless steel brackets, however ceramic and polymeric brackets are widely used and less often brackets made of Au or Ti alloys. The archwires most commonly inserted are made of stainless steel or nickel-titanium alloys, however beta-titanium and cobalt-chromium-nickel archwires are available in the market. The 300-series stainless steel alloys used for the construction of most orthodontic attachments belong to the austenitic family. These alloys offer better corrosion resistance and are nonferromagnetic because of their fcc crystal structure. "Austenitizing" elements (Ni, Mn, and N) are added in order to preserve the highly corrosion-resistant solid solution phase even at room temperature². These elements enhance corrosion behavior, however it's the addition of Cr that has the greatest effect on corrosion resistance³. The balance between austenite-ferrite-martensite often is unstable and extensive cold work may turn these steels into ferrite or martensite². The AISI type 316L austenitic stainless steel is the most commonly used orthodontic bracket and archwire material. It is composed (wt%) of 0.08 carbon, 2.00 manganese, 0.045 phosphorus, 0.03 sulfur, 0.75 silicon, 16 to 18 chromium, 10 to 14 nickel, and 2 to 3 molybdenum, with the remainder being iron^{4,5}.

NiTi alloys are used widely in Orthodontics, mainly in form of archwires for the initial leveling phase of treatment. There are two major NiTi phases in these wires: the austenitic phase occurs at high temperatures and low stresses and has an ordered base-centered cubic

(bcc, cesium chloride type) structure. The martensitic phase NiTi forms at low temperatures and high stresses and has been reported to have a distorted monoclinic, triclinic, or hexagonal structure. The alloy used for these wires consists of 55% Ni and 45% Ti (approx. and may contain small amounts of Cu or other elements)⁶.

The orthodontic applications of alloys are unique in that the alloy element is not implanted into the tissue, as in cases of orthopedic implants, but is placed in the open oral cavity.

Therefore, the implantation tests that are frequently used in other medical fields bear no relevance to the clinical use of orthodontic materials. These materials (ie, wires, brackets) exhibit a pattern of continuous reaction with the environmental factors present in the open oral cavity, in contrast with the implanted materials, whose reactivity is decreased because of the formation of a connective tissue capsule surrounding the foreign body³. The aim of this review is to discuss this continuous reaction of the orthodontic appliances with the environmental factors and present the major adverse effects of their metallic and polymeric components.

Alloys in Orthodontics

Corrosion

Corrosion occurs intraorally regardless of the alloys' metallurgic structure and manufacturing defects may accelerate the process². Corrosion resistance property of the stainless steel is owed to chromium and depends on a passive film, which spontaneously forms (passivation) in air and under most tissue fluid conditions. This film also contains Fe and Ni. Mo provides further protection from crevice and pitting corrosion. Oxygen is necessary to form and maintain the film, whereas acidity and chloride ions can be particularly detrimental to it. Stainless steel is characterized by a passive-active behavior depending on the environmental

conditions in which the protective chromium oxide layer may be eliminated (active form) or regenerated (passive form)³. Corrosion of NiTi alloys is not so well understood than corrosion of stainless steel. The corrosion resistance feature of the former wires is largely due to the presence of a large proportion of Ti (48%–54%), which forms several oxides upon exposure to air, including TiO₂, TiO, and Ti₂O₅, with TiO₂ being the most common and stable one^{3,7}. The chromium oxide passive films of the stainless steel alloys are less stable as their titanium oxide counterparts and as a result the Ti alloys have superior corrosion resistance than stainless steel, particularly in environments containing chloride anions^{6,8}.

Orthodontic materials are placed in contact with biologic tissues or fluids and the formation of organometallic compounds is enhanced by local micro-environmental factors, including pH fluctuations and temperature variants, a fact that might increase the corrosion rate of the alloy⁹. Corrosion of the orthodontic bracket-archwire complex has received attention after the corrosion products of the bracket base were shown to be diffused into the adhesive¹⁰. The complexity of the materials and interfaces involved contributes to the development of corrosion in various elements of the appliance. The engagement of the wire into the slot with stainless steel or elastic ligatures formulates an environment in which many forms of corrosion can develop¹¹.

Galvanic corrosion. This type of corrosion is more common in the broader dental applications of materials. If the potential difference between two types of metals is high enough, a galvanic corrosion is formed and the less stable metal tends to corrode and releases ions into the solution as it disintegrates⁷. For example, a traditional bracket is composed of 2 phases: a low modulus of elasticity stainless steel alloy for the manufacturing of the base, which presumably allows for easy debonding after treatment, and a high modulus steel alloy for the wings, which minimizes deformation caused by the engagement of the wire and ensures stress transfer from the activated archwire or the prescribed bracket slot to the tooth^{11,12}. The wing alloy is more

vulnerable to corrosion because of the presence of copper in its composition. Addition of Cu increases its hardness, however it has an adverse effect on corrosion resistance. This wing alloy is less noble than the 316 SS, which is commonly used for the manufacturing of the bracket base⁴.

The parts of an orthodontic appliance may be joined by brazing alloys of nickel, silver, or gold^{11,12}. Different brazing materials are used for the different brands, and thus different performances are expected during intraoral exposure¹³. The practitioner should pay attention to the composition of soldering silver-based alloy and more particularly to the quantities of copper and zinc. Intraorally aged Ag soldering alloys used in space maintainers demonstrated substantially increase in surface roughness and significant Cu and Zn reduction, a fact that may raise biocompatibility concerns¹⁴. Orthodontic soldered appliances should be well polished to limit ionic release to its minimum¹ and gold-based brazing materials should be preferred. However, these materials may lead to dissolution of stainless steel, which is less noble than the gold alloys^{4,15}. Laser welding and metal injection molding (MIM) may overcome these issues. MIM brackets are one-piece appliances with uniform elemental distribution and show lack of galvanic corrosion, but have higher porosity and are made of one alloy type, which does not satisfy the requirements for stiffer wing component and compliant base^{15,16}. However, at least a MIM bracket type produces similar potential differences to a conventionally manufactured bracket (two parts, base and wing) with NiTi archwires in vitro. Ti brackets have been found to be single-piece appliances or consist of two separate parts jointed together by laser welding¹⁷. CuNiTi archwires were less susceptible to galvanic corrosion in comparison with conventional NiTi with both bracket types, MIM and conventional¹⁸.

Apart from the galvanic couples within a bracket, all attachments in the presence of metallic archwires provide the essential conditions for the development of a galvanic couple. In vitro

experiments have shown that archwires were consistently the cathode and the brackets were the anode of the galvanic cell. As a result, brackets undergo accelerated corrosion in order to protect archwires¹⁸. Nevertheless, the corrosion rates of stainless steel and NiTi are increased in acidic environments¹⁹.

Uniform attack arises from the interaction of metals with the environment and the subsequent formation of hydroxides or organometallic compounds. It is the most common type of corrosion, occurring with all metals at different rates and may not be detectable before large amounts of metal are dissolved³.

Pitting corrosion affects brackets and wires and may take place before intraoral placement since excessively porous surfaces have been found on as-received products³. A pit is considered as a pore with a depth equal to its width. Although MIM brackets, as single-unit appliances, are free from the galvanic corrosion that occurs between the bracket and brazing alloys in conventional brackets, their increased porosity may augment their tendency towards pitting corrosion¹⁶.

Crevice or gasket corrosion occurs in loci exposed to corrosive environments, often through the application of nonmetallic parts on a metal (ie, elastomeric ligatures on a bracket). It arises from differences in metal ion or oxygen concentration between the crevice and its vicinity. The attack may be attributed to the lack of oxygen associated with plaque formation and the byproducts of microbial flora, which disturb the regeneration of the passive layer of chromium oxides²⁰. In retrieved brackets, the depth of the crevice may even reach 2–5 mm, perforating its base. The 2205 alloy demonstrates substantially less crevice corrosion than the 316L alloy when coupled with NiTi, β -Ti, or stainless steel archwires in vitro^{2,5}.

Intergranular corrosion affects mainly the solubility of chromium carbide and is due to the precipitation of chromium carbide at the boundaries of the grains²¹.

Fretting corrosion refers to the process occurring in contact areas of materials under load and finds its analogue in the bracket's slot-archwire or archwire-stainless steel ligature interfaces. It involves the cold welding at the interfaces under pressure, which results in rupturing of the contact points (Fig. 1).

Microbiologically influenced corrosion occurs on orthodontic adhesives and composite resins which may results in the formation of craters in the bracket base^{22,23,24}. Additionally, salivary enzymes are capable of softening the surface of dimethacrylate polymers presumably by inducing a hydrolysis of methacrylate ester bonds. Thus, mechanical removal of the softened surface layer is easier and will expose a new surface layer vulnerable to enzymatic attack²⁵.

Stress corrosion during function may develop due to electrochemical potential differences that occur from the generation of tensile and compressive stresses. These stresses are developed locally because of the multiaxial, three-dimensional loading of the wire after the insertion into the bracket slots.

Corrosion fatigue occurs in materials left in the intraoral environment for extended periods of time under load. Orthodontic wires or the inner arch of the headgear facebow wires entering the buccal tube are most frequently affected²⁶. Aging of orthodontic alloys due to repeated cyclic stressing is accelerated by the reduction in fatigue resistance induced by exposure to a corrosive medium such as saliva (corrosion fatigue). The process is characterized by the smoothness of the fractured areas^{3,27,28}

Release of substances

In the early stages, efforts to study the release of substances from orthodontic materials consisted of measuring in vitro and with primitive techniques (weight, morphology) the ions

or monomers released in the immersion media. Later, the same method was complemented with the introduction of instrument analysis such as atomic emission or absorption spectroscopy for metals. High-performance liquid chromatography and gas chromatography–mass spectroscopy were also used for the qualitative and quantitative analysis of immersion media, saliva, blood, or urine with respect to the concentrations of polymer by-products^{11,29}. In vitro quantification of the metallic content of biologic fluids, including saliva, blood, and urine, cannot withstand any level of scrutiny regarding methodological soundness of the approach. In these cases, a plateau in the release rate is reached rapidly because of the establishment of equilibrium between the metal ions in the solution and the metal ions at the metal-solution interface. This leads to the false conclusion that the release rate is accelerated initially and remains steady later. However, most studies show that aging of the alloy in the form of fatigue or corrosion enhances ionic release^{3,7}. In vitro studies do not take into account clinical factors such as fretting corrosion due to bracket-archwire ligation and the corrosive action of the intraoral flora and plaque accumulation. In vivo study of nickel levels in the saliva of orthodontic patients assumes that ionic release has a steady pattern and that the concentration at that specific time represents the release for the full term of treatment. Retrieval analyses, estimating indirectly metallic content in new, used, and recycled specimen may overcome these methodological problems³⁰.

The salivary metal levels of patients undergoing orthodontic treatment do not exceed those of daily intake from food and air²⁹. The release of metal ions from stainless steel orthodontic attachments and wires mainly involves iron, chromium, and nickel. Part of the corrosive products may be adsorbed by enamel or moved to the gastrointestinal track during normal swallowing. Although all 3 elements can have adverse effects, nickel has received the most attention because of its reported potential for hazardous effects^{31,32}. In the austenitic steels that contain Ni as the primary austenite stabilizer, the Ni atoms are not strongly bonded to form some intermetallic compound. As a result, the likelihood of in vivo slow Ni ion release from

the alloy surface is increased, which may have implications for the biocompatibility of these alloys³. The 2205 stainless steel has lower nickel content (4 to 6 wt%) than the 316L stainless steel (10-14 wt%) and could be an alternative for orthodontic brackets⁵. The formation of oxide layer may inhibit the outward movement of ions, thereby acting as an obstacle for release³². Retrieval analyses provide critical information on the service history and alterations of materials, even from the attack of specific microbial species. Elemental analysis of in vivo-aged brackets (retrieved, and recycled) has shown that Ni release occurs under clinical conditions³⁰. Fatigue of the alloys results in acceleration of release rates and disintegration reactions⁷.

Additionally, Ni may be released from the widely used NiTi archwires. Ni content was not found to differ between as-received and retrieved NiTi after an intraoral service period of 4 months, suggesting an absence of nickel release. However, Ni release cannot be excluded from these analyses, since the loss of macroparticles due to surface wear and delamination phenomena does not alter the overall elemental composition of the material. Additionally, galvanic couples occur between the stainless steel wire and the components of the bracket may have an unpredictable outcome on the corrosion susceptibility of the wire alloys in vivo³². In vivo, it was demonstrated that Nickel concentrations in saliva increased after placement of stainless steel bands and brackets but decreased to approximately the starting levels 2 weeks after placement of the bands and brackets. Afterwards, Nickel leaching occurred after placement of the Ni-Ti archwires. This effect decreased within 10 weeks³³.

There is an abundance of evidence supporting the carcinogenic, mutagenic and cytotoxic actions of Ni in cell cultures. Ni was found to have carcinogenic action both, in pure form and in compounds (with chloride and sulfide formulations)³⁴. These findings should be interpreted with caution, because documented toxicities generally apply to the soluble forms of these elements. In an in-vitro immersion study, the ions released from stainless steel and NiTi

brackets and wires were found to have no measurable effect on the viability and physiology of PDL and gingival fibroblasts³¹. However, in vitro protocols always fail to properly simulate clinical conditions. Currently, any association between release of metal and any metabolic, immunologic, or carcinogenic toxicity is conjectural; cause and effect have never been demonstrated in humans²¹. There are several alternative Nickel-free materials available for substitution of the Nickel-containing orthodontic materials (Tab. 2).

Ti brackets were evaluated in an immersion study regarding ionic release. It was demonstrated that the released Ti levels were below the threshold level (1 ng/ml) of analysis whilst traces of Al and V were found in the immersion media. However, long-term release may be higher than that occurring within the first weeks, and therefore, studies employing time intervals within the 1 month range for the investigation of ionic release suggest a low margin for safety³⁵.

High noble dental alloys are used more rarely in Orthodontics. The most important characteristics of these alloys are the tarnish and corrosion resistance in the oral environment. Gold, palladium, and platinum have low labilities and are unlikely to be released at high levels³⁶. Alloy chemistry appears to be the major factor determining alloy corrosion resistance, which is best assured by high nobility, that is high gold content. Corrosion in gold alloys occurs primarily in silver-rich regions and secondarily in copper-rich regions. 'Low-gold' casting alloys are characterized by decreased chloride corrosion resistance, when compared with ADA Type III (hard gold alloy with minimum 75% Au+ platinum group metals content) and Type IV gold alloys (extra hard gold alloy with minimum 75% Au+ platinum group metals content)³⁷. Tarnish response is not solely dependent upon nobility. Other factors such as the environment, ratio of elements in the alloy and heat treatment can alter the alloy's tarnish resistance. However, a high silver:copper ratio is favorable^{38,39}.

Oral hygiene is essential since the action of microbial colonization is twofold: (1) certain species can take up and metabolize metals from alloys and (2) microbial byproducts and the metabolic processes may alter the conditions of the microenvironment (ie, decreasing the pH, thereby contributing to the initiation of the corrosion process)³. Some species may adversely affect the surface structure of dental alloys and endodontic silver points among other materials. It is known that sulfate-reducing and nitrate-reducing bacteria are aggressive and inflammatory to the hosting tissues, and that these bacteria also affect the corrosion processes of various alloys^{40,41}.

Demineralization

The prolonged presence of the attachments of orthodontic appliances on the enamel surface in the oral environment has been associated with the development of some unfavorable sequelae in the form of demineralization of hard dental tissues in cases of patients with poor oral hygiene. Fluoride is the most potent cariostatic agent available that can prevent caries, and the present guidance provides recommendations to have this as a central concept. Many fluoridated materials at different stages may be used, such as bonding (primers, glass ionomer cements and resin-modified glass ionomer cements) and during treatment (rinsing solutions, gels, and varnishes^{42,43,44}. However, bond strength of the fluoride-releasing orthodontic bonding agents is substantially lower than those of conventional resins^{45,46}. Moreover, the long-term beneficial effect of fluoride releasing adhesives has not been sufficiently established for some applications such as glass ionomer cements or fluoride-releasing resinous adhesives, since most of the fluoride is released within the first few days or weeks^{11,44,47,48}. Daily intake of probiotic lozenges was not found to affect the development of WSL during orthodontic treatment with fixed appliances⁴⁹. Peptides such as a statherinlike

peptide have been found to reduce the rate of hydroxyapatite demineralization in caries-simulating solutions by about 50%; research efforts have also focused on salivary proteins, which can bind to hydroxyapatite surfaces and form a selectively permeable pellicle⁵⁰. Management of post-orthodontic white spot lesions is based on remineralization strategies or minimal-invasive camouflage of the lesions, micro-abrasion and resin infiltration. The latest systematic review points out that there is a lack of reliable scientific evidence to support one technique over the other⁵¹.

Polymers

Degree of cure

Dental polymers are not inert in the oral environment, and may release several components, initially due to incomplete polymerization, and later due to degradation. Two monomers are mainly used in orthodontic adhesive resins: bisphenol A diglycidyl dimethacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) (Tab. 2). The former is used in the majority if not all of the currently used orthodontic adhesives⁵². These methacrylate monomers may be released after polymerization, depending on its extent, even after 1 year⁵³.

Polymerization efficiency or degree of cure is considered an essential property for all polymers. In dental composite resins, this variable has been found to modulate the physical, mechanical, and biologic properties of the material, since a poor polymer network is susceptible to the release of biologically reactive substances (monomers and additives), predisposes to water absorption and swelling and hydrolytic degradation, and is associated with reduced mechanical properties^{54,55,56,57}. Apart from liberating unreacted monomers, monomer degradation releases metabolic by-products, including triethylene glycol (TEG),

methacrylic acid (MA), 2,3-epoxymethacrylic acid (2,3-EMA) and formaldehyde which induced comparable toxic effects as the raw comonomer⁵⁸. Formaldehyde is a very reactive chemical presenting cytotoxic, mutagenic, carcinogenic and pro-allergenic potential⁵⁹. It results from the oxidation of pendant C=C and could be released from dental composite resins even after 4 months of immersion in water⁶⁰.

The degree of conversion is closely related to the polymerization shrinkage of resin composites and both mechanisms are manifestations of the same process. Dental composites would ideally show an optimal degree of conversion and minimal polymerization shrinkage⁶¹. Residual monomers are responsible for increased bonding failures and can also cause adverse biologic effects, showing allergic, cytotoxic, mutagenic, and estrogenic characteristics⁶². It was demonstrated that in dental composites, as the percentage of monomer conversion increased, cellular toxicity decreased⁶³. Even a non-lethal concentration of TEGDMA (that can be easily attained after diffusion across the dentin) has anti-proliferative properties by delaying the cells at the G2 phase of the cell cycle⁶⁴. Intraoral aging was shown to affect the setting status of an orthodontic resin composite and a glass ionomer adhesive, relative to control specimens stored in water. The latter showed significantly lower degrees of cure than did the retrieved specimens. Intraorally aged specimens showed enhanced oxidation of residual carbon-carbon bonds in the composite and slightly increased dissolution of the weaker calcium-salt phase in the glass ionomer cement⁶⁵.

In light-cured monomers, the extent of polymerization depends on several factors, including exposure time, photoinitiator concentration, light intensity emitted by the curing unit at the peak absorbance wavelength of the photoinitiator, and filler volume fraction⁶⁶. Light-cured adhesives show decreased oxygen inhibition of polymerization, shorter polymerization reaction, and extended working time, which allows for extended handling in the positioning of bracket, thus being ideal for educational purposes. A further advantage of these adhesives

over the 2-phase systems is the decreased formation of formaldehyde. Mixing and handling of the 2-phase systems increase oxygen inhibition of the polymerizations reaction and accordingly the formaldehyde levels.

Additionally, better peripheral bracket sealing is obtained with light-cured composites compared with chemically cured systems. However, both systems seem not to induce acute cytotoxic reaction to human periodontal ligament fibroblasts, whereas a minor cytostatic effect was demonstrated, implying a potential biologic concern⁶⁶. The degree of conversion is particularly important for fixed retainer adhesives, since they remain in the oral cavity for longer periods than the bracket adhesives and a greater surface area is exposed. Liquid composite resins have the highest leaching potential, since leaching decreases with increasing filler content, followed by liquid-paste systems and paste-paste formulations⁶⁷. Higher monomer concentrations were eluted from a chemically cured adhesive than from a visible light-cured orthodontic adhesive⁶⁸. Direct (through the bracket) irradiation of stainless steel brackets bonded to the visible light-cured adhesive showed higher monomer elution than indirect irradiation (from the incisal and cervical bracket edges). Low degrees of cure were found in self-etching resin cements, a fact that raises questions as to whether these materials can be successfully used in clinical applications, where light attenuation takes place⁵⁷.

Bisphenol-A release

Bisphenol-A (BPA) is a synthetic compound used in the manufacturing process of some of the monomer systems of orthodontic resins. Recently, the release of BPA in the oral cavity has received wide interest in the orthodontic literature⁶⁹. Its hormone-related effects have been demonstrated but there is no high-level studies available in this area and the evidence on this topic is based on observational in-vivo and in-vitro studies. This is even more critical in cases

of fixed lingual retainers, where the composite resin remains exposed to the oral cavity to a greater extent than the bracket bonding adhesive. A light-cured bracket adhesive used to bond lingual fixed retainers released BPA in vitro even after 1 month⁷⁰. Therefore, recommendations have been suggested regarding clinical practice and standardization of the research methods in the future.

- Light-cure tip should be kept as close to the adhesive as clinically possible,
- pumice prophylaxis after bonding might reduce the potential for BPA release,
- indirect irradiation (around the bracket edges) should be used instead of direct irradiation (through the bracket),
- patients should rinse their mouths during the first hour after bonding, in order to prevent exposure to the potential hazard of leaching monomers^{71,72},
- it is advisable to use adhesives especially designed for fixed retainers.

In the light of these concerns, several BPA-free orthodontic adhesives have been introduced, mainly based on aliphatic dimethacrylates. Recently, an experimental BPA-free resin composite adhesive for retainer bonding was developed. After laboratory comparison between this adhesive and a commercially available product based on BPA components, the authors conclude that this may be used as an alternative in the clinical practice⁷³. Further efforts have been made to replace Bis-GMA with UDMA in orthodontic adhesives. The latter lacks benzoic rings, and thus potential release of BPA and concomitantly xeno-estrogenic action⁵². Nevertheless, the absence of the BPA structure does not essentially imply the lack of estrogenic activity, since several BPA-free chemicals used as replacement for BPA containing resins have been shown to trigger an estrogenic effect⁷⁴.

BPA is released after placement of some dental pit and fissure sealants in the oral cavity⁷⁵. The biggest quantities are detected in saliva immediately after or one hour after their placement⁷⁶. Polycarbonate-based composite brackets may induce estrogenic effects, and

furthermore some of them show specific cytotoxic effects and release substances that activate mitochondrial apoptosis after 3 months storage in water⁷⁷. In a prospective cohort study, it was shown that the aesthetic nickel-titanium arcwires lost a significant amount of coating, even 1 month after insertion⁷⁸. The biological properties of the detached fraction of coating remain to be clarified.

Removal of adhesives

The cleanup of the enamel surface after the removal of the orthodontic attachments involves grinding of the adhesive layer with rotary instruments at low or high speed. This process produces aerosol containing polymer matrix and filler degradation byproducts as well as particulates arising from the wear of bur, which may have potentially hazardous action on the respiratory system and estrogenicity^{79,80}. Grinding especially without water spray, increases the temperature locally, with unpredictable effects on the composition and formation of resin byproducts. Preventive measures should be applied in daily practice, such as mask and protective glasses, access to fresh air, and use of suction. Mechanical removal of as much resin as possible before using rotary instruments is suggested¹⁵. This barrier equipment should be used in order to prevent aerosol contamination too⁸¹.

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Tables

Table 1. Nickel-containing orthodontic materials and the corresponding Nickel-free substitutes³.

<i>Category</i>	<i>Material</i>	<i>Ni-Free Substitute and Modifications</i>
<i>Standard appliances</i>	Brackets	Ni-free stainless steel, ceramic, plastic, Ti, gold-plated, or coated with other precious metals (Pd, Pt) brackets
	Bands	Gold-plated bands
<i>Treatment utilities</i>	Stainless steel archwires	No alternative currently available; development of composite wires in progress
	NiTi archwires	coated NiTi archwires; b-Ti archwires; a-Ti archwires
	CoCrNi archwires (Elgiloy)	No alternative currently available
<i>Mechanics auxiliaries</i>	Sliding yokes, transpalatal and lingual arches	b-Ti, plastic, or inert metal (gold) coating of wire segments
<i>Miscellaneous auxiliaries</i>	Stainless steel ligatures	Teflon-coated ligatures
	Kobayashi hooks	Teflon-coated Kobayashi hooks, Ni-free brackets with hooks
	Coil springs	Elastomeric ligatures
<i>Fixed expansion appliances</i>	Stainless steel appliances (Quad- Helix, Rapid Palatal Expander)	b-Ti (TMA) wires for Quad-Helix
	Stainless steel headgear	Teflon-coated stainless steel facebow
	NiTi spring screws	No alternative currently available
<i>Removable appliances</i>	Stainless steel components of Hawley appliance and variations	Plastic or elastic retainers; elastic positioners or acrylic splints, Invisalign technique
<i>Complex therapeutic interventions</i>	Orthognathic surgery lag screws and plates	Resorbable polylactic-polyglycolic lag screws and plates
	Distraction osteogenesis apparatus	No alternative currently available

Table 2. Polymers used in Orthodontics.

Bonding materials	Bis-GMA, TEGDMA
Aesthetic orthodontic wires	coated NiTi wires (polytetrafluoroethylene or rhodium coating) or composite wires (reinforced polymers)
Thermoplastic aligners, Essix, Invisalign	polyurethane
Brackets	Polycarbonate, polyurethane, polyoxymethylene
Lip bumper	Polypropylene
Hawley appliance	Methyl Methacrylate

Figure legend

Fig.1. Fretting corrosion in contact areas between ligatures-archwires under load.

